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**Automated Discovery of Complex Reaction Networks Reaction**

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UNIVERSITY OF WASHINGTON**

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## **Automated Discovery of Complex Reaction Networks: Reaction Topology, Thermochemistry and Kinetics**

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**ABSTRACT:** Understanding the combustion mechanism of jet fuel is essential for the design of stable, responsive, and highly efficient military jet engines. However, this is a challenging mission because of extreme conditions such as high temperature, supersonic incoming airflow, short lifetime of intermediates, the complexity of combustion reaction networks, and the difficulty to identify important reaction channels in combustion chemistry. In the present work, a physics-based approach (i.e., ab initio dynamics) was utilized to guide the enumeration and characterization of chemical reaction networks in combustion, minimize human input, and avoid on-the-fly thermochemical estimation. Based on the enumerated elementary reactions, a framework that is able to automatically reduce negligible species and elementary reactions was suggested and hence optimized reaction networks were generated. The methodology was applied to study methanol oxidation, prediction of ethylene combustion mechanism and transition states of different types of chemical reactions.

## 1. Introduction

Obtaining more powerful, stable and responsive jet engines is always an essential need for the nation. One important component of meeting this need is for researchers is to discover and understand combustion mechanism of jet fuel in extreme conditions such as supersonic incoming airflow and high temperature. This is a challenging task because of short lifetime of intermediates, the complexity of combustion reaction networks, challenges in identifying important reaction channels in combustion chemistry, and severely lacking experimental methods and devices that are able to detect and monitor a significant fraction of reactions in such extreme conditions.

To explore combustion mechanisms, scientists have made extensive efforts and great progress. For example, Smith et al. provided the GRI mechanism for natural gas combustion with a complete set of elementary reactions.<sup>1</sup> The researchers of the LLNL combustion projects have kept producing full mechanisms of different hydrocarbon fuels for over thirty years.<sup>2-4</sup> Researchers have also developed different methods and algorithms to obtain important reaction channels. For instance, Broadbelt et al. suggested a matrix-based reaction network generator NETGEN with rate-based algorithm to optimize reaction channels.<sup>5-7</sup> Green and co-workers developed Reaction Mechanism Generator (RMG) to produce the full combustion mechanisms of fuel, and applied rate-based algorithm and sensitivity analysis to predict important reaction pathways.<sup>8</sup> Similarly, there are combustion reaction network generators such as COMGEN, EXGAS, and KING appearing recently as well.<sup>9</sup> All these reaction network generators, although each of them has distinguishing features, share common characteristics and generally include following modules: a unique topological representation of a chemical compound, an explicit representation of reaction rules, a generation scheme through the application of reaction rules, and a gauge to optimize (reduce) the complex reactions networks.<sup>9</sup> Human inputs like reaction rules and the method for optimization of reaction networks are required for all these reaction network generators. In addition, to predict reaction pathways, on-the-fly high-level quantum calculations are often needed for the estimation of thermochemical and even kinetic data. Based on these reasons mentioned above, a physics-based approach (i.e., ab initio dynamics) was suggested to guide the enumeration and characterization of chemical reaction networks in combustion and minimize human inputs and avoid on-the-fly thermochemical estimation. Furthermore, a framework that is able to automatically reduce negligible species and elementary reactions was suggested and hence optimized reaction networks were generated.

In the present work, Car-Parrinello molecular dynamics (CPMD)<sup>10</sup> in conjunction with Metadynamics (MetaD) using social permutation invariant (SPRINT) coordinates as collective variables, as the physics-based approach mentioned above, was utilized to generate combustion network. CPMD is a planewave-based ab initio molecular dynamics method, which has been extensively used to study chemical reactions because of its faster computational capability than BOMD (Born-Oppenheimer molecular dynamics)<sup>11</sup> and reliability.<sup>12</sup> To overcome the simulation time scale problem for chemical reactions, the enhanced sampling method MetaD was chosen to accelerate the exploration on potential energy surfaces because



of its wide and successful applications to chemical reactions.<sup>12-14</sup> Meanwhile, the SPRINT coordinates were selected as generic reaction coordinates because it was originated from graph theory and includes global topological information of all atoms' coordinates in the system. It seems to have ability to explore all reaction channels by solving eigenvectors of contact matrix of the system.<sup>15</sup>

By using the biased CPMD approach with SPRINT coordinates this AFOSR project allowed us to investigate three specific research areas: methanol oxidation, ethylene combustion, and transition state searches for different chemical reactions. The results were used to verify the practicability of the suggested physics-based approach. And hopefully the approach can be extended to study and predict combustion mechanism of jet fuel in extreme conditions in the future.

## 2. Methodology and Computational Details

The CPMD v3.15.1 software package<sup>10,16</sup>, combined with PLUMED v1.3,<sup>17</sup> was used to run all Metadynamics<sup>18,19</sup> molecular simulations. The MetaD technique was selected to accelerate sampling of rare events.<sup>18</sup> In summary, MetaD forces reactants to react within the underlying phase space of specific degrees of freedom by adding a history-dependent Gaussian-shaped bias potential on coarse descriptors known as collective variables (CVs). Typically, for using MetaD to study chemical reactions very specific CVs related to the researchers' hypotheses about how a reaction will happen are inputs at the onset of the simulation.

The choice of CVs is a key issue in MetaD simulations. Of particular importance for generating combustion reaction networks is the requirement that the CVs must be non-specific because what kind of chemical reactions will happen are not predefined, and can be driven to explore all elementary chemical reactions and reaction channels by adding bias on them to explore a FES. To satisfy this requirement, we used the SPRINT coordinates,<sup>20</sup> which include the information of all atoms' relative orientations and distances to define the topology of the system based on graph theory<sup>20-22</sup>, as the CVs in CPMD simulations.

The numbers of starting configurations of interested systems were set large enough so that sufficient sampling of different collision pathways were able to produce major reaction channels. All elementary reactions and channels were summarized and generated based on all parallel CPMD simulations.

## 3. Discussion and Results

To monitor the time evolution of various species during combustion and verify the capabilities of the suggested approach to enumerate elementary reactions, a series of fuel + oxidation molecules simulations were set up, run, and investigated. And the results were summarized.

First, with 30 random O<sub>2</sub> configurations relative to the position and orientation of CH<sub>3</sub>OH, 1CH<sub>3</sub>OH + 1O<sub>2</sub> simulations were performed to observe the methanol oxidation process. This effectively allowed including various stochastic effects in the system since, unlike using transition state theory, the outcomes of biased CPMD simulations potentially could be dependent on starting configurations via a collision

trajectory.

Figures 1 and 2 demonstrate the chemical reactions might be recorded by monitoring the potential energy (the Kohn-Sham energy) and the changes in the SPRINT coordinates of involved atoms. Clearly, the first energy potential energy barrier is for the bond fission of C-O in methanol as shown in Figure 1, and  $\bullet\text{CH}_3$  radical is crucial to activate the stable  $^3\text{O}_2$  molecule. In Figure 2, around time 9 ps, all the SPRINT coordinates are in a narrow range, which shows that the reactants  $\text{CH}_3\text{OH} + \text{O}_2$  are close to each other. At time around 10.0 ps, the carbon SPRINT coordinate drops first due to the C-O bond fission, then increase by 1 because of the formation of  $\text{CH}_3\text{OO}\bullet$  radical. Similarly, at time 21.5 ps,  $\bullet\text{HO}_2$  is close to  $\bullet\text{CH}_2\text{OH}$  radical and  $\text{CH}_2\text{O} + \text{H}_2\text{O}_2$  are formed, therefore their SPRINT coordinates curves are close to each other again. In fact, we can observe that the SPRINT coordinates characteristically change along with chemical reactions in all 30 simulations.

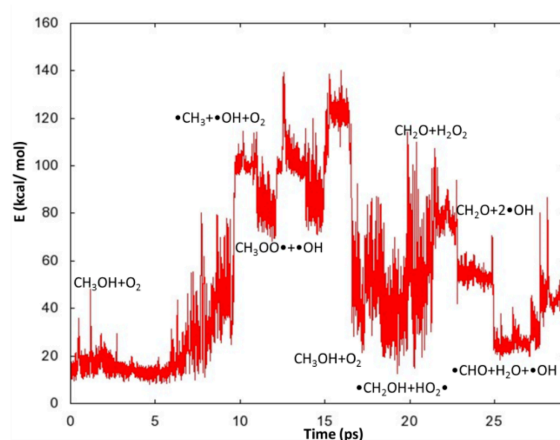


Figure 1. The time evolution of elementary reactions and Kohn-Sham energy of one simulation (#2) at temperature 1000K.

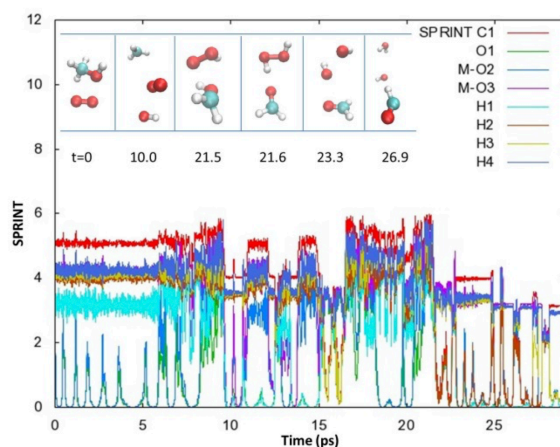


Figure 2. Time evolution of SPRINT coordinates of one simulation (#2), and 6 snapshots at key time steps. M-O is a designation for the two atoms initially present as molecular oxygen.

To investigate the properties of biased CPMD with SPRINT coordinates simulations for methanol oxidation, the major stable species were tracked during the simulations. As shown in Figure 3, the counts summarized from all 30 simulations of selected interesting species were monitored. The motivation for the aggregate

simulations was to attempt and obtain a general picture about what the MetaD trajectories are revealing about methanol oxidation given that the biased CVs are totally generic about the types of transformations that could happen. Several striking features can be perceived from analysis of the evolution of each of the simulations. Oxidation of carbon-containing species is gradually observed, and in a production simulation time of 24 ps all fuel molecules completely react with oxygen in all simulations. As shown in Figure 1, following methyl radical, the methylperoxy ( $\text{CH}_3\text{OO}\cdot$ ) are the largest carbon-containing intermediates observed and play crucial roles for succeeding reactions. In the later stages of the simulations, a mixture of radicals such as  $\cdot\text{CHO}$ ,  $^3\cdot\text{CH}_2$ ,  $\cdot\text{CH}_3$ ,  $\cdot\text{OH}$ ,  $\text{HO}_2\cdot$  and  $\text{H}\cdot$  appear. Both formaldehyde and formyl radical are produced in relatively large amounts, suggesting they could be a gateway between the substrate and final products  $\text{CO}_2$ . It is also noteworthy that hydroxyl radical, regarded as an important species in combustion chemistry, is always existing with quite stable large amount (around 15) in the production runs. In the meantime, the numbers of  $\text{H}\cdot$  and  $\cdot\text{CHO}$  steadily increases while the number of water regarded as a quenching molecule in combustion keeps growing. Also notable is that the number of hydroperoxyl ( $\text{HO}_2\cdot$ ) radicals is quite stable.<sup>15</sup>

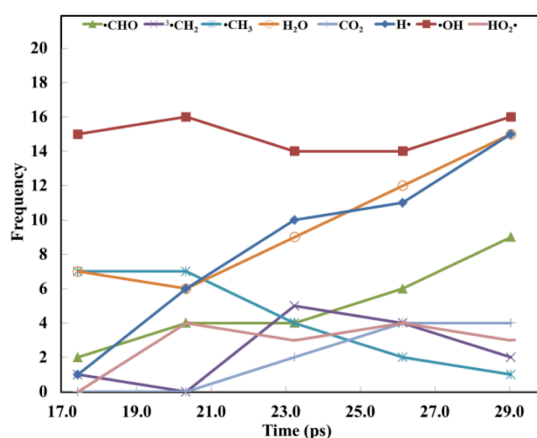


Figure 3. The cumulative time evolution of count numbers of selected products ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) and radicals with largest count numbers ( $\cdot\text{CHO}$ ,  $^3\cdot\text{CH}_2$ ,  $\cdot\text{CH}_3$ ,  $\text{H}\cdot$ ,  $\cdot\text{OH}$ ,  $\text{HO}_2\cdot$ ) in the 30  $\text{CH}_3\text{OH}+\text{O}_2$  simulations from time 17.4 to 29.0 ps.

To further test the practicability of the new method in combustion science, ethylene combustion was selected as the target since there are still some open questions about its mechanism although experimental and theoretical scientists have extensively studied it. For example, Konnov and Xu found the discrepancies of four suggested ethylene combustion mechanisms.<sup>23</sup> By studying this simplest but important alkene with the new approach, the re-discovered mechanism of ethylene combustion was to explain the conflicts among the previous four mechanisms for same fuel, and therefore verify the practicability of the suggested physics-based approach.

Three model systems with different stoichiometry: 1ethylene+1 $\text{O}_2$ , 1ethylene+2 $\text{O}_2$ , and 2ethylene+1 $\text{O}_2$  were set up for CPMD simulations. The temperature was set at 1000K. By combining all simulations results with different stoichiometry, the overall reaction network was generated as shown in Figure 4. The total connections (reactions)



and carbon-containing species are 386 and 116, respectively. Clearly, even considering the most fuel-rich condition (2ethylene+1O<sub>2</sub>), it was confirmed that the C2 (2 carbon atom containing) and C1 compounds like CH<sub>2</sub>CHO, CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>, CHO and CH<sub>3</sub>, are dominant in the reaction network despite of so many C3 and C4 compounds such as C<sub>3</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>6</sub> formed in ethylene rich conditions.

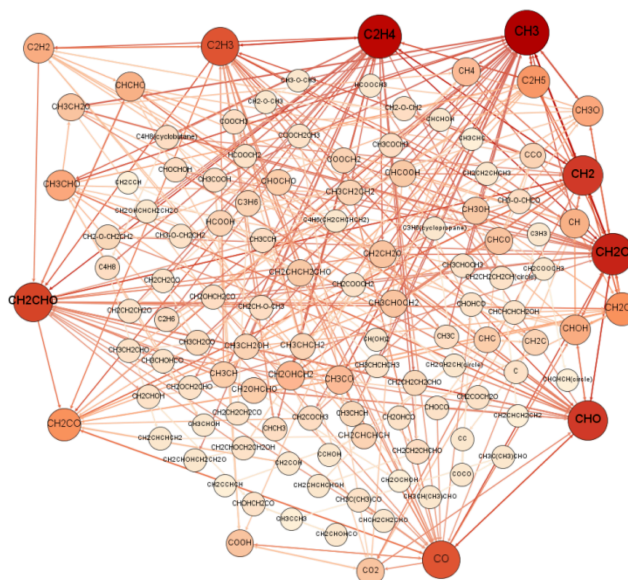


Figure 4. The overall graph of flux of carbon-containing species of three (1C<sub>2</sub>H<sub>4</sub>+1<sup>3</sup>O<sub>2</sub>, 1C<sub>2</sub>H<sub>4</sub>+2<sup>3</sup>O<sub>2</sub>, 2C<sub>2</sub>H<sub>4</sub>+1<sup>3</sup>O<sub>2</sub>) simulation results at temperature 1000K. The area and color of circles represent the connectivity of different carbon species: the larger/darker areas have more connections. A bidirectional arrow denotes that a two-way reaction is observed.

Besides the combustion chemistry study, because of the unique character of the new approach, i.e. the ability to identify reaction pathways by monitoring the potential energy ( $E_{KS}$ ) and topological descriptors specific reactants/products, it is naturally to apply the new approach to detect transition states for different chemical reactions.

A well-studied chemical reaction between CH<sub>3</sub>CH<sub>2</sub>F and F<sup>-</sup> in gas phase<sup>24,25</sup> were investigated using the new approach. There are 6 possible reaction channels<sup>24</sup> and S<sub>N</sub>2 nucleophilic substitution CH<sub>3</sub>CH<sub>2</sub>F\* + F<sup>-</sup> = CH<sub>2</sub>CH<sub>2</sub>F + F\*<sup>\*</sup> (\* denotes the substituted fluorine atom) reaction is one of them. Without specifying which atoms were involved in the reactions (i.e., specifying system-dependent CVs), 20 biased CPMD simulations with SPRINT coordinates, set up with different initial configurations, were run. All six channels were successfully reproduced within the parallel simulations. The time profiles of the SPRINT coordinates and Kohn-Sham energy of one simulation are shown in Figure 5. At the beginning the SPRINT coordinate of the F atom (F2) periodically oscillates between 3 and 4, and the SPRINT coordinate of the anion F<sup>-</sup> between 0 and 3; at time about 1.05 ps the SPRINT coordinates of the anion fluorine (aF1) are close to 3 while the corresponding Kohn-Sham energy has a local maximum (the black circle). The transition state structure for S<sub>N</sub>2 reaction was

therefore predicted and captured as shown in Figure 5. The captured TS structure from CPMD simulations were verified by directly inputting them into a saddle point search in Gaussian, further validated by confirming the presence of one imaginary frequency, and coupled with IRC calculations to verify the correct reactants/products were found. Compared to Gaussian 2009 MP2/aug-cc-pVDZ obtained TS structure, the CPMD obtained geometry agrees well with MP2 results, having RMSD 0.02 Å for S<sub>N</sub>2 TS structures.

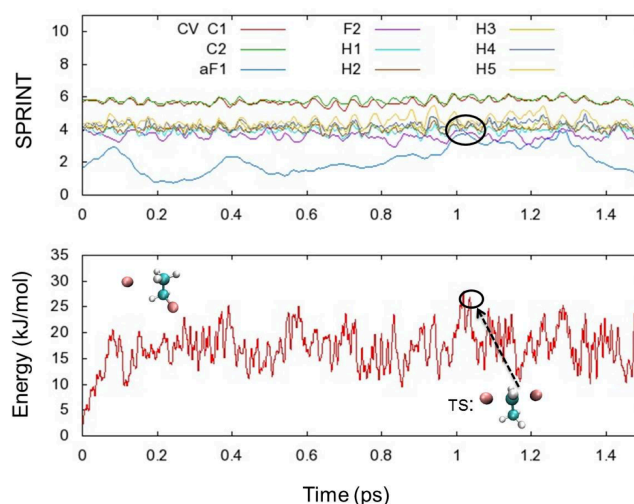


Figure 5. The time evolution of SPRINT coordinates and Kohn-Sham energy of a S<sub>N</sub>2 reaction  $\text{CH}_3\text{CH}_2\text{F}^* + \text{F}^- = \text{CH}_3\text{CH}_2\text{F} + \text{F}^*$  at 400K. ‘aF1’ in the top figure denotes the anion F<sup>-</sup>. At around time 1.05 ps, the reaction happens.

## Conclusions and Remarks

Using the biased ab initio method, the current available results show that it is possible to systematically enumerate all elementary reactions in the simulations of fuel combustion, generate the reaction networks with carbon-containing species, and optimize them and obtain the combustion mechanisms. For example, by solving the conflicts among the previous ethylene combustion mechanisms, a framework that minimizes human input and maximizes predictive capabilities has been created.

By correctly identifying transition state structure of  $\text{CH}_3\text{CH}_2\text{F}^* + \text{F}^- = \text{CH}_2\text{CH}_2\text{F} + \text{F}^*$  SN2 reaction, it shows that the suggested method is an exciting addition to the list of potential uses for the new SPRINT CVs, and paves the way for simultaneously exploring both the interatomic connectivity in complex reacting system (i.e., a chemical reaction network) along with accurate representations the relevant transition states that connect stable states in the systems’ PESs. By applying the SPRINT coordinates and a TS identification scheme to chemical reactions, the new approach seems show potential to recognize TS state structure accurately.

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**Abstract**

ABSTRACT: Understanding the combustion mechanism of jet fuel is essential for the design of stable, responsive, and highly efficient military jet engines. However, this is a challenging mission because of extreme conditions such as high temperature, supersonic incoming airflow, short lifetime of intermediates, the complexity of combustion reaction networks, and the difficulty to identify important reaction channels in combustion chemistry. In the present work, a physics-based approach (i.e., ab initio dynamics) was utilized to guide the enumeration and characterization of chemical reaction networks in combustion, minimize human input, and avoid on-the-fly thermochemical estimation. Based on the enumerated elementary reactions, a framework that is able to automatically reduce negligible species and elementary reactions was suggested and hence optimized reaction networks were generated. The methodology was applied to study methanol oxidation, prediction of ethylene combustion mechanism and transition states of different types of chemical reactions.

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29. S. Zheng, J. Pfaendtner, "Car-Parrinello Molecular Dynamics + Metadynamics Study of High-Temperature Methanol Oxidation Reactions Using Generic Collective Variables", J. Phys. Chem. C., 2014, 118(20), 10764-10770.

+2 additional in preparation

### Changes in research objectives (if any):

There was a change in focus of the model system from ionic liquid high temperature chemistry to hydrocarbon chemistry due to the change in supervising program from Molecular Dynamics to Combustion and Energy Sciences.

### Change in AFOSR Program Manager, if any:

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